

KOH CONCENTRATION EFFECT ON THE CYCLE LIFE OF NICKEL-HYDROGEN CELLS III. CYCLE LIFE TEST

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Summary

A cycle life test of Ni/H₂ cells containing electrolytes of various KOH concentrations and a sintered-type nickel electrode was carried out at 23 °C using a 45 min, accelerated, low earth orbit (LEO) cycle regime at 80% depth of discharge. One of three cells containing 26% KOH has achieved over 28 000 cycles, and the other two 19 000 cycles, without a sign of failure in this accelerated cycle life test, which is still in progress. Two other cells containing 31% KOH electrolyte, which is the concentration presently used in aerospace cells, failed after 2979 and 3620 cycles in the same test. This result indicates that the cycle life of the present type of Ni/H₂ cell may be extended by a factor of 5 - 10 simply by lowering the KOH concentration from 31% to 26%.

Introduction

Long cycle life of a Ni/H₂ battery at high depth-of-discharge operation is desired, particularly for an LEO spacecraft application. Typically, battery life of about 30 000 cycles is required for a five-year mission in an LEO. Such a cycle life with presently available cells can be assured only at a very low depth-of-discharge (below 40%) operation [1]. Previously, in an effort to develop a long life nickel electrode for Ni/H₂ cells, we studied various design parameters of the electrode. Those studies included evaluation of the effects of plaque pore size, mechanical strength, and active material loading level on the cycle life of the electrode [2 - 4]. Although the variations in these parameters significantly affected the cycle life, improvement over the present aerospace standard electrodes was relatively small. In a continuing effort, we began to investigate the effects of KOH concentration in the electrolyte on the cycle life [5]. This paper is a progress report of this study: results already show that the cycle life of an Ni/H₂ cell is tremendously improved simply by using an electrolyte of lower KOH concentration (26%) rather than a state-of-the-art value of 31%.

Test cells and life test cycling regime

The average theoretical capacity of the test cells was 7.3 A h, as calculated from the amount of active material without correcting for the amount of cobalt additive. Each cell capacity was rated at 6.24 A h. Therefore, C rate for these cells equals 6.24 A.

The cycle life test was carried out at 23 °C by continuous cycling to 80% depth-of-discharge of the rated capacity in a 45 min cycle regime. This cycle regime was a 2.74 C rate discharge for 17.5 min, and a 27.5 min charge at 1.92 C rate for 110% recharge. The life tests of cells BP1 - BP6 began ten months earlier than cells BP7 - BP10. The cycling test was interrupted periodically for capacity measurements — at approximately every 1500 cycles. The end-of-charge voltages (EOCV) and pressures (EOCP), and end-of-discharge voltages (EODV) and pressures (EODP) of each cell were measured daily (every 32 cycles). This cycling test was continued to the failure point, at which the value of the EODV dropped to 0.5 V.

Two different failure criteria, EODV values of 0.9 and 0.5 V, were used to define the cycle life of the cell. The value 0.9 V represents the utilization of only the main discharge voltage plateau, while 0.5 V represents the utilization of the total cell capacity, including that of the second voltage plateau, which occurred at about 0.8 V. (This second discharge voltage plateau will be discussed later.) The KOH concentration of the electrolyte of individual test cells and the cumulative life test status of the test cells are shown in Table 1. Further details of the test cell design and life test conditions were reported earlier [5].

TABLE 1

KOH concentrations in electrolyte and cycling status of Ni/H₂ test cells at 80% depth of discharge

Cell no.	[KOH] (%)	No. of cycles to 0.9 V	No. of cycles to 0.5 V	Cycling status
BP1	21	5047	> 27000	in progress
BP10	23.5	4803	> 18000	in progress
BP2	26	> 27000	> 27000	in progress
BP9	26	> 18000	> 18000	in progress
BP3*	26	4329	9241	removed
BP4	31	2979	3275	removed
BP5	31	3620	4230	removed
BP6	36	1268	1845	removed
BP7	21	1037	6508	removed

*Teardown analysis of this cell showed that there was a mechanical defect in tab-welding on one of the hydrogen electrodes.

Life test results

The cumulative EODVs of the cells are plotted against the number of life cycles in Figs. 1 and 2. The cell with 36% KOH failed by the 0.9 V criteria after 1268 cycles, while two cells with 31% KOH cycled for 2979 and 3620 cycles. However, all three cells containing 26% KOH electrolyte (BP2, 8, and 9) are still being cycled without a sign of failure, accumulating over 19 000 and up to 28 000 cycles. (One of the four 26% KOH cells (BP3) had a mechanical defect in tab-welding on one of the hydrogen electrodes.) These results indicate that the cycle life of an Ni/H₂ cell is greatly increased as the KOH concentration is reduced in each 5% step (36% - 31% and 31% - 26%). The improvement in cycle life with the concentration change in the latter step is especially remarkable.

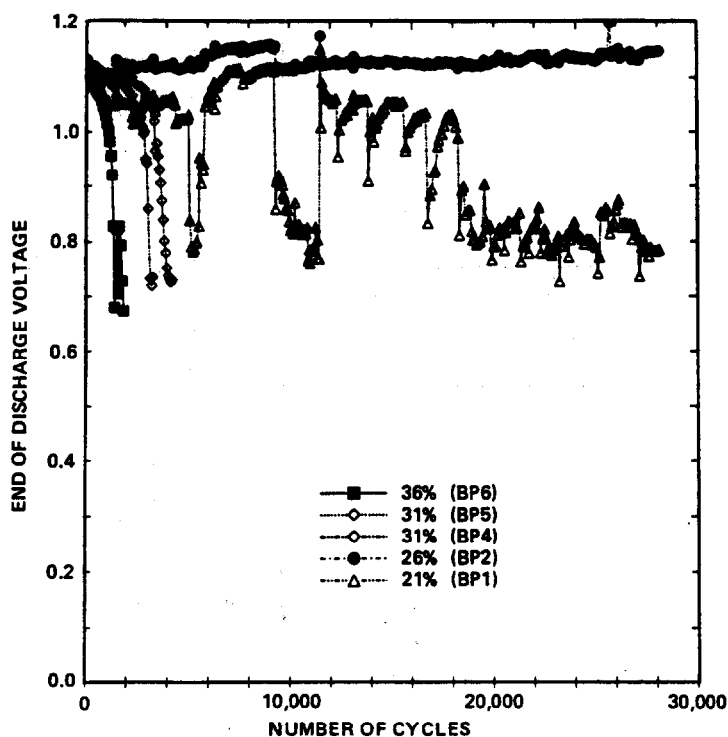


Fig. 1. Plots of the EODV vs. cycle number for Ni/H₂ cells (BP1 - BP6) with various KOH concentrations. All cells were cycled at 80% depth-of-discharge except for the cycles between 5785 and 9209, when the depth-of-discharge value was 74%.

The cycle life change, however, appears to be complicated when the KOH concentration is further decreased below 26%: the value of the EODV of BP10 (23.5% KOH) decreased below 0.9 V after 4800 cycles. The value remained at about 0.8 V for several thousand cycles before it began to rebound after about 10 000 cycles. The BP10 cell recovered its initial EODV value after about 15 000 cycles, indicating that the capacity was increased

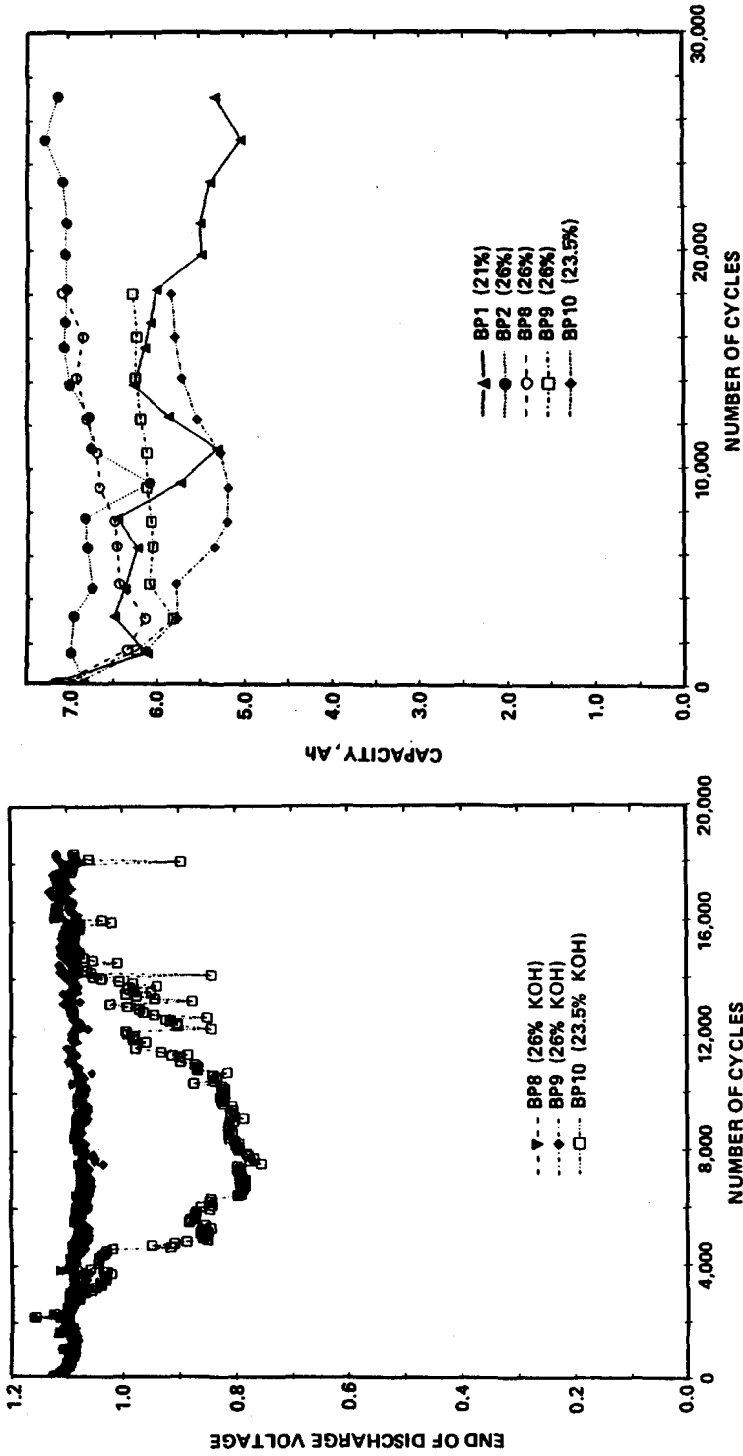


Fig. 2. Plots of the EODV at 80% depth-of-discharge vs. cycle number for Ni/H₂ cells (BP8 - BP10) with various KOH concentrations.

Fig. 3. Plots of interim capacity values (second measurement) of Ni/H₂ cells with various KOH concentrations vs. cycle number. The capacities were measured by charging the cells at C rate for 80 min and then discharging them to 1.0 V at 1.37 C rate.

rather than being decreased with cycling, as shown in Fig. 2. BP1, which contained 21% KOH, had cycled 5049 times when its EODV went below 0.9 V, and BP1 has presently accumulated over 28 000 cycles. The EODV of this cell was unstable during the test, although values became more or less stable at about 0.8 V after 20 000 cycles, as shown in Fig. 1. The changes of EOCV, EOCP, and EODP of these cells were discussed previously [5].

Duplicate or triplicate interim capacity measurements of all test cells were made out after roughly every 1500 cycles by charging the cells at C rate for 80 min and then discharging them at 1.37 C rate to 1.0 V. The capacity values of the first measurements after the cycle interruptions were slightly different from (usually larger than) those of subsequent measurements, while the second and the third usually agreed with each other. The differences are probably due to the cycling history at a higher rate than that at which the capacity is measured. The values of the cell capacity from the second measurement are plotted against the cycle number in Fig. 3. These changes in capacity are generally consistent with the EODV changes, as expected from the nature of their interrelationship. All the cells with 26% KOH electrolyte showed consistently higher capacity than those with the lower KOH concentrations. The discharge voltage curves of these interim capacity measurements are shown in Figs. 4 and 5.

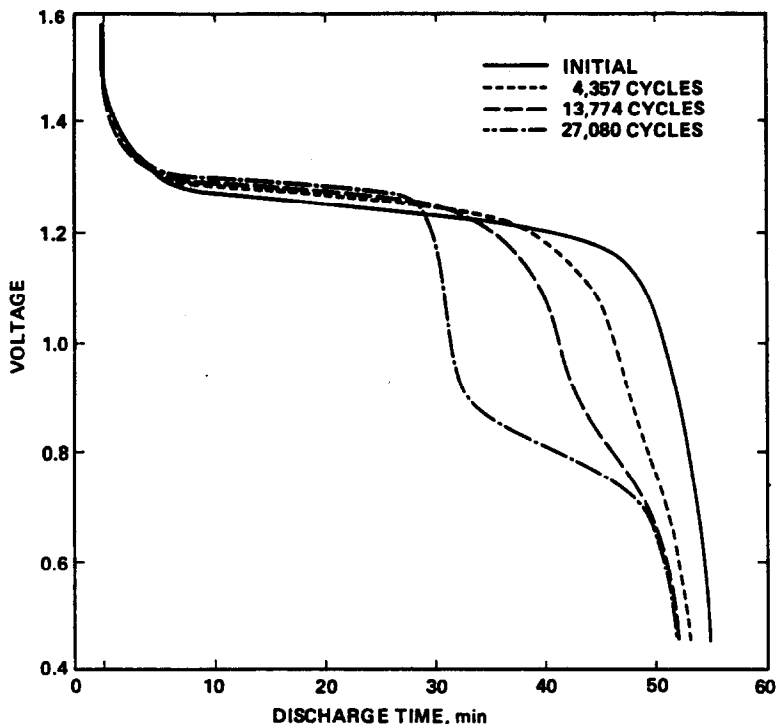


Fig. 4. Discharge voltage traces of BP1 during interim capacity measurements at various life cycles.

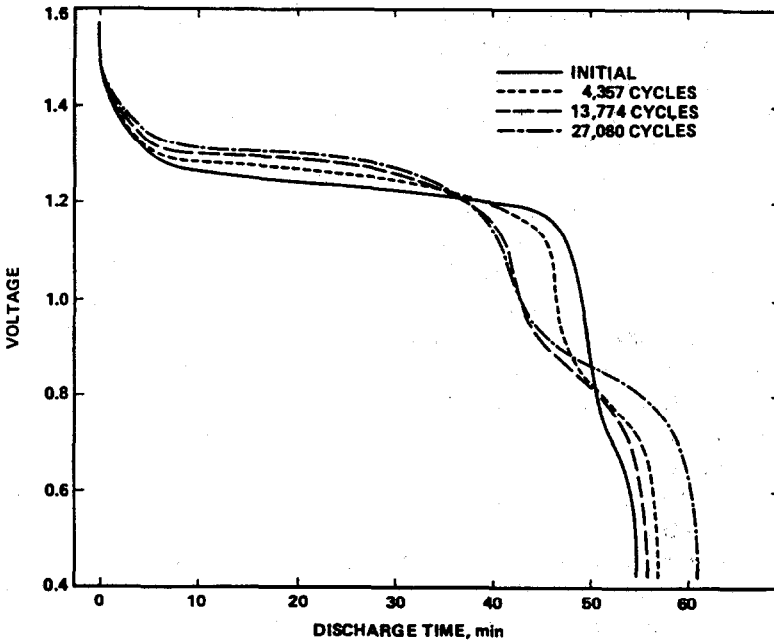


Fig. 5. Discharge voltage traces of BP2 during interim capacity measurements at various life cycles.

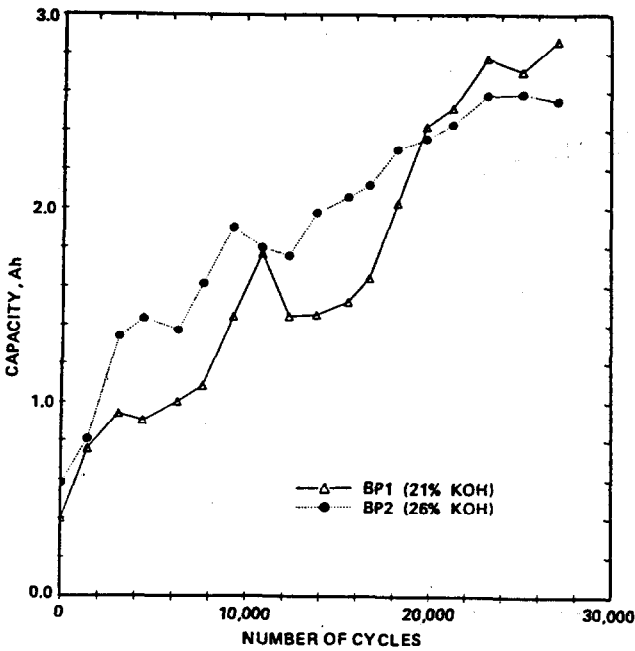


Fig. 6. Plots of the second discharge voltage plateau capacities vs. cycle number. These capacities were calculated by the difference between the capacity values to 0.5 V and 1.0 V.

The main voltage plateau capacity (to 1.0 V) of BP1 decreased with cycling, as shown in Figs. 3 and 4, while the second voltage plateau capacity (about 0.8 V) increased. Total capacity, including the second voltage plateau capacity (to 0.5 V), remained almost unchanged, as shown in Fig. 4. The stable, low EODV of this cell over the last several thousand cycles recorded in Fig. 1 is due to this second plateau capacity. The main voltage plateau capacity of BP2 remained almost constant after an initial decrease over the first several thousand cycles (Fig. 3), while the second voltage plateau capacity increased steadily with cycling in a rate similar to that of BP1, as shown in Fig. 6. The overall capacity of this cell increased with cycling. This increase is probably caused by gradual plaque corrosion, which creates additional active material.

Another noticeable aspect of the discharge voltage curves is that the discharge voltage of the main plateau increased gradually with cycling, as shown in Figs. 4 and 5. This voltage shift and the second plateau phenomena are not fully understood at the present time, and studies of these phenomena are planned as part of the failure analyses.

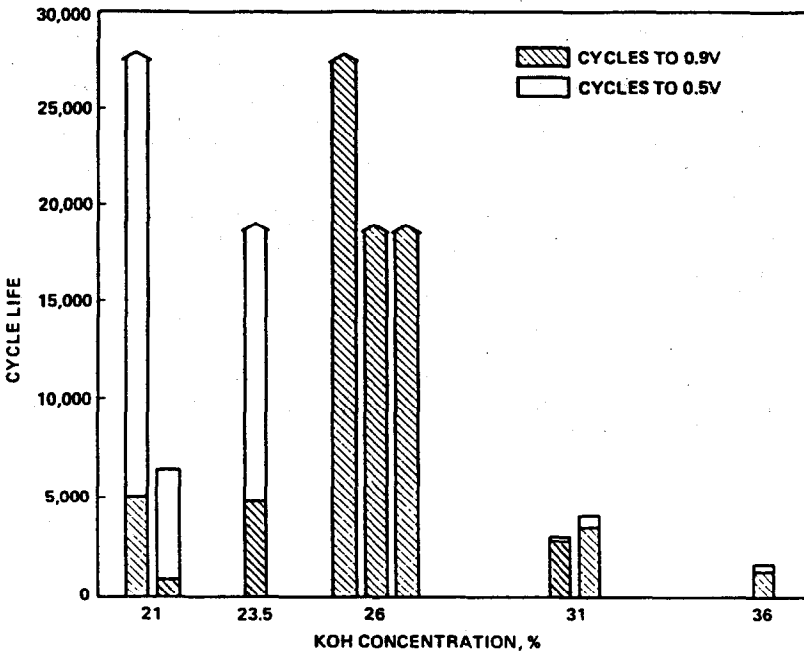


Fig. 7. Comparison of cycle life of Ni/H₂ boiler plate cells containing various KOH concentrations.

Conclusion

The cycle life of an Ni/H₂ cell in the accelerated test increased greatly as the KOH concentration in the electrolyte was decreased from 36% to 26%. The cycle life improvement on using 26% KOH instead of the present

aerospace standard of 31% is tremendous, as shown in Fig. 7. This cycle life improvement should not be discounted on the basis that the initial capacity of the cell decreases slightly with the decrease in KOH concentration, as reported earlier [5], because all the test cells in this study were rated at the same capacity value (6.24 A h) independent of the KOH concentration used. However, the cycle life effects in further reducing KOH concentration below 26% are not clear, because of observed erratic behavior at concentrations of 23.5% and 21%.

Acknowledgement

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